PATENT SPECIFICATION (11) 1 534 667

(54) A PROCESS FOR RECOVERING H2 FROM A GAS MIXTURE

(71) We, BERGWERKSVERBAND GmbH. a German Body Corporate, of 351 Frillendorfer Strasse. Essen, Germany, do hereby declare the invention, for which we

5 pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:–

The invention relates to a process for

10 recovering H2 from gas mixtures that contain at least one of the two gases N2 and CO in addition to H2 and CH4 and possibly higher hydrocarbons, CO2 and trace impurities such as O2, NOx, H2S, COS, mer-

15 captans, NH3 and steam/water vapour, by means of adsorption, if necessary at elevated pressure, in an adsorber filled with a carbonaceous adsorption agent, in which CH4 and if present higher hydrocarbons, CO2

20 and the said trace impurities are adsorbed in the outlet region (second zone), whereas H2 leaves the adsorber, and in which the adsorbed gases are desorbed at uniform time intervals by reducing the pressure.

25 The production of hydrogen with concentrations above 95 volume %, mostly even above 99 volume %, from gas mixtures which contain methane, higher hydrocarbons, CO2, CO and N2 in addition to hyd-

30 rogen, by adsorption and desorption on an adsorption agent, has been known for a long time. The gas mixtures are derived mainly from steam-reforming plants, ethylene plants, ammonia cracking plants, catalytic-

35 reforming plants and chloralkali electrolysis plants. Before the hydrogen recovery these gases are often subjected to a preliminary purification in which for example H2S, COS, mercaptans and steam/water vapour are

40 removed.

The recovery of hydrogen is very largely carried out on adsorption agents, such as for example on zeolitic molecular sieves or activated charcoals, and is effected in the fol-

45 lowing manner: all ths afore-mentioned gases with the exception of H2 are adsorbed at generally elevated pressure, while hydrogen leaves the adsorber as product gas. Before any of the adsorbed gases, with the exception of H2, has reached the end of the 50 adsorber, the latter is regenerated and the gas stream is led during this time through a second parallel adsorber.

As is known, in the adsorber the adsorption fronts of weakly adsorbably. gases 55 advance more rapidly from the inlet to the outlet than is the case with strongly adsorbable gases. Moreover, the weakly adsorbable gases are displaced for the most part from their adsorption sites by the strongly 60 adsorbable gases. For these reasons, there is a specific adsorption zone for each gas in the adsorber, the zone of the most strongly adsorbed gas being at the adsorber inlet.

Regeneration (desorption) is carried out 65 in the following manner: the pressure in the adsorber is first of all reduced, in fact generally to normal pressure, though the pressure may be reduced to the vacuum range. During this pressure reduction the adsorber can 70 in principle also be heated. However, little use is made of this possibility since the heating up and subsequent cooling to the adsorption temperature require a considerable amount of time. As a result, the adsorbers 75 must be built on a very large scale, which involves a considerable additional expenditure with regard to energy costs. Isothermal adsorption and desorption are therefore generally preferred. In addition to pressure 80 reduction, desorption using a scavenging gas is also employed.

It has however been found that regeneration by pressure reduction is not sufficient to produce pure hydrogen. residual amounts 85 of, in general, CH4, higher hydrocarbons, CO2 and possibly trace impurities remain on ths adsorption agent, which are displaced by gas flowing through in the renewed adsorption stage following regeneration, and con- 90

taminate the hydrogen obtained. A sufficient regeneration has however been obtained hitherto by inserting a scavenging step between the pressure reduction and renewed adsorption in order to displace and desorb the said residual amounts.

This scavenging can be carried out for example with part of the obtained product hydrogen. This gives a complete desorption of the remaining residual amounts. In order to be able to scavenge out the various residual amounts in as short a time as possible, the scavenging is conveniently carried out countercurrent to the adsorption. The great disadvantage of this scavenging is principally the fact that a not inconsiderable amount of the hydrogen is lost as product gas. This is even the case if the scavenging is carried out at relative low pressures.

It has also been proposed (see German Offenlegungsschrift 17 69 936 and German Auslegeschrift 20 38 261) to use not product hydrogen for the scavenging but a part of the desorption gas formed by pressure reduction in the regeneration. In is nevertheless still necessary to use some pure product hydrogen at the conclusion of the scavenging, and also to effect the pressure build-up to the adsorption pressure with pure hydrogen. The latter is carried out, like the scavenging, in countercurrent to the adsorption direction in order to displace back to the inlet of the adsorber the residual amounts still remaining during scavenging with desorption gas. The fact that the adsorbers are only partially utilised in these cases a further disadvantage.

Very ofte it is necessary to build a scavenging gas reservoir in order to have available scavenging gas, whether it be product hydrogen or hydrogen-rich desorption gas, and this involves additional expense as regards apparatus.

It is furthermore known from German Offenlegungsschrift 15 44 009 that the adsorbers can be utilised as a scavenging gas reservoir by using the desorption gas of one adsorber for the time being to scavenge the other adsorber. However, in order to be able to produce hydrogen continuously it is necessary to operate at least three adsorbers or even four adsorbers, in which the stages of adsorption, pressure reduction, scavenging and pressure build-up occur in succession. In this connection, the pipework involved in connecting the adsorbers to the inlets and outlets of the desorption gases for the scavenging is extremely costly.

What is desired is to produce hydrogen at concentrations above 95 volume %, preferably above 99 volume %, from gases that contain at least one of the two gases N_2 and CO in addition to H_2 and CH_4 and possibly higher hydrocarbons, CO_2 and possibly the said trace impurities, by adsorption and desorption, while largely avoiding the afore-mentioned disadvantages.

The mixtures may be derived from the plants already mentioned in the introduction (steam-reformers, catalytic-reformers, ammonia gas plants, etc.), for example in the case where no conversion, or only a partial conversion, of CO to CO_2 is carried out. Further important gases which can be used in the invention are product gases from coal coking or coal gasification plants. After preliminary purification such gases have for example the following typical concentrations:

from coking: 55 % H_2, 24 % CH_4, 11 % N_2, 6 % CO,
2 % higher hydrocarbons, 2 % CO_2,

from gasification: 54 % H_2, 20% CO, 18 % CO_2, 7 % CH_4,
1 % higher hydrocarbons.

If the preliminary purification of the coking gases simply involves the components such as ammonia, hydrogen sulphide and benzene which can be relatively easily removed by washing, as well as constituents which condense out readily, such as for example tars, then the gas mixture for the hydrogen recovery still contains traces of O_2, NO_x, H_2S, COS, mercaptans, NH_3 and water vapour. Such a gas mixture is described herein as a non-highly purified coking gas.

According to the invention, there is provided a process for recovering H_2 from a gas mixture which contains H_2 and CH_4, at least one of the two gases N_2 and CO and possibly one or more higher hydrocarbons, CO_2, and trace impurities by passing the gas mixture into an adsorber filled with a carbonaceous adsorption agent, in which the CH_4, and the higher hydrocarbon(s), the CO_2, and said trace impurities, if present, are adsorbed in a first zone in the inlet region of the adsorber, and the N_2 and/or CO are adsorbed in a second zone in the outlet region of the adsorber, whereas H_2 leaves the adsorber, and in which the passage of the gas mixture to be adsorbed is interrupted at uniform time intervals for desorbing the adsorbed gases by reducing the pressure in the adsorber, the gas mixture containing not less than 5 volume % N_2 and/or CO, the change from adsorption to desorption taking place at the latest when the second zone has diminished to a length of 30% of the overall adsorber length, but before the first breakthrough of the N_2 and/or CO, and the desorption being carried out, while the adsorber outlet is closed, by evacuating the adsorber from the adsorber inlet, whereby CH_4 and the higher hydrocarbon(s) if present, the CO_2, and the said trace impurities if present, are scavenged by N_2

and/or CO desorbed in the second zone, and by unadsorbed H_2 present in the second zone.

The great advantage of the invention is that only one adsorber is required to carry out the individual process steps of adsorption, pressure reduction and scavenging, and this means that no further adsorbers or indeed any additional reservoir with the relevant inlet and outlet pipes for the scavenging gas are necessary. Two adsorbers connected in parallel in which the processes of adsorption and desorption (pressure reduction and scavenging) take place alternately will obviously be employed with regard to a continuous gas recovery, but this is quite general in adsorption technology. If the pressure reductio is carried out by release of pressure and subsequent evacuation, then, as is known, three adsorbers will be used to provide a better utilisation of the vacuum pump.

Fig. 1 is intended to illustrate the invention in more detail, and shows the two adsorption zones in the adsorber resulting from the basically known different adsorption capabilities of the individual gases in the equilibrium state. When in the adsorption stage the adsorption fronts have reached the indicated positions in the adsorber, with pure hydrogen flowing out (the positions can easily be detected by analysis), the pressure is reduced countercurrent by release of pressure and evacuation. The gases contained in the second zone, namely N_2 and-or CO, are used directly to displace and scavenge CH_4, higher hydrocarbons (C_nH_m), CO_2 and possibly the afore-mentioned trace impurities, in the same adsorber. This takes place particularly effectively and with the desired high purification effect if the linear velocities in the adsorber are adjusted to below 10 cm!sec during the pressure reduction. These advantageous gas velocities for the scavenging process can be established by suitably dimensioning the adsorber cross-sections, the pipeline cross-sections, the vacuum pump and, if necessary, by incorporating regulable flow control valves.

However, a decisive factor with regard to the success of the scavenging is that the gas mixture must contain the components N_2 and/or CO in a total volume of at least 5 volume %. It was in fact established that no satisfactory desorption of CH_4, higher hydrocarbons, CO_2 and possible aforementioned trace impurities can be obtained in the absence of these gases. If necessary, the required minimum concentration of 5 volume % in the gas mixture must be obtained by adding N_2 and/or CO.

It was also surprisingly found that in order to produce hydrogen of high purity it is merely necessary to carry out a practically complete scavenging of the first region in the first zone in which CH_4, higher hydrocarbons, CO_2 and possibly the afore-mentioned trace impurities are adsorbed. Scavenging is not necessary to desorb N_2 and/or CO, although these gases are present in a relatively high concentration of at least 5 volume %, in order to obtain hydrogen in concentrations above for example 99.9 volume %, since they are desorbed purely by reducing the pressure.

The following can be said concerning the length of the two zones. It was found that the desorption of the adsorbed gases in the first zone is only complete if the second zone comprises not less than 30 % of the overall adsorber length. It is perfectly in order for this zone to be even longer, for example to constitute 50 % of the adsorber length. The length of the two zones is governed, inter alia, by the type of adsorption agent. When using activated charcoals, a length ratio of zone 1 : zone 2 of 50 : 50 can be established without any difficulty. It can also be varied by choosing special carbonaceous adsorption agents, such as for example carbonaceous molecular sieves. In the cass of zeolites the ratio is displaced more in the direction 70 : 30. These relations apply to normal pressures and temperatures. The length ratio of the two zones can also be varied by altering these parameters. By using these measures it can easily be ensured in all cases thah the second zone constitutes not less than 30 % of the adsorber length.

The desorption that takes place after the conclusion of adsorption produces a pressure of $150 - 1$ mm Hg, preferably $50 - 10$ mm Hg in the adsorber. The desorption end pressure influences the purity of the hydrogen produced during the subsequent renewed adsorption. It has been found that at higher end pressures (about 150 mm Hg) the hydrogen contains larger amounts of N_2 and/or CO ($\geqslant 1$ %), while at lower end pressures (< 50 mm Hg) the proportions fall to far less than 1 % and even to less than 0.1 %. CH_4, higher hydrocarbons, CO_2 and possibly the aforementioned trace impurities are of course no longer contained in any case in the product hydrogen since they are always scavenged by N_2 and/or CO.

Before a new adsorption stage can begin it is desirable, just as with the known processes, to raise the pressure in the adsorber by introducing hydrogen at a pressure of 1 atmosphere.

It has moreover surprisingly been found that when using carbon molecular sieves with average micropore diameters – measured by methanol adsorption – of 0.4 to 0.55 nm as adsorption agent and with adsorption times of not more than 20 minutes, preferably not more than 10 minutes, the aforementioned trace impurities in coking gases

and similar gases are also removed from the feed-stock gas and can also be desorbed from the adsorption agent by the described process. This is all the more surprising, especially as such trace impurities cause, as is known, resin formation in the adsorption agent as a result of cracking or polymerisation, and can then scarcely be desorbed by simple pressure reduction. The indicated maximum times for adsorption and desorption should not be exceeded. It is not possible to give a lower limit however since the desorption of, in particular, the said trace impurities is improved by shorter cycle times. Of course, profitability considerations place a lower limit on adsorption and desorption times.

Example 1.

A gas having the following composition: 54.5 %, 11.5 % N_2, 6.1 % CO, 24.3 % CH_4, remainder:

higher hydrocarbons and CO_2

is passed through an adsorber containing 0.5 ·1 of activated charcoal at 21°C and an adsorption pressure of 15 atmospheres. Until the N_2 breakthrough is reached after 6 minutes, hydrogen flows out at a constant pressure of just under 15 atmospheres and in a purity of ah least 99.9 volume %. At the end of the adsorption stage the concentration profiles in the adsorber are similar to those in Fig. 1. The second zone occupies rather more than half the adsorber length.

The pressure in the adsorber is then released to 1 atmosphere within 1.5 minutes, in the opposite direction to the adsorption direction, and following this is reduced to 30 mm Hg by means of a vacuum pump. Motor-driven, regulable control valves are located between the vacuum pump and adsorber and also in the pressure release line, by means of which the desorption can, if necessary, be regulated in such a way that the linear gas velocities in the adsorber do not exceed 10 cm/sec. After 4 minutes the pressure has fallen below 30 mm Hg and the desorption is finished.

Pure hydrogen is next introduced into the adsorber until a pressure of 1 atmosphere is reached. A new adsorption is carried out by introducing gas mixture at a pressure of 15 atmospheres. No interfering impurities, which might originate from a residual content of impurities, could be determined in the outflowing hydrogen before the N_2 breakthrough was reached after 6 minutes. Even after 10 and more adsorption and desorption cycles the hydrogen produced has a purity of more than 99.9 volume %.

It was established that these purities are not longer obtained with very high desorption velocities. From a large number of tests and experiments it has been found that the upper limit is approximately 10 cm/sec.

Example 2.

The test described in Example 1 is carried out at an adsorption pressure of 21 atmospheres and with the following gas:

54 % H_2, 20 % CO, 18 % CO_2, 7 % CH_4 and 1 % higher hydrocarbons.

The adsorption is discontinued after reaching the CO breakthrough, as long as hydrogen at a purity of 99.9 % still flows out. Regeneration is then carried out as in Example 1. In this case also, no interfering impurities in the hydrogen (99.9 %) could be detected after many adsorption and desorption cycles. If the desorption is completed at 100 mm Hg instead of 30 mm Hg, hydrogen purities of almost 98 % are obtained. The remainder is basically CO.

Example 3.

A model gas mixture not in accordance with the invention and consisting of 75 % H_2 and 25 % CH_4 – i.e. without any N_2 and/or CO – is introduced into an activated charcoal adsorber having a volume contents of 250 ml, at 1 atmosphere until the CH_4 front has reached 70 % of the adsorber length traversed by the gas mixture. During this time pure hydrogen flows out. The adsorber is then evacuated down to 30 mm Hg in countercurrent to the adsorption, the linear gas velocities being less than 10 cm/sec. Finally, further model gas mixture is introduced at 1 atmosphere in the original flow direction. Immediately the adsorption pressure is reached and as soon as gas begins to flow out from the adsorber, CH_4 occurs in a concentration of at most 3.5 volume % in the hydrogen. This does not change even if a pressure equalisation with pure hydrogen at 1 atmosphere is carried out before introducing the model gas. A CH_4 residual charge clearly remains on the activated charcoal after the desorption, and undesirably contaminates the hydrogen produced.

If on the other hand a scavenging gas, e.g. hydrogen, is passed towards the end of the desorption at a pressure of 100 mm Hg and a linear gas velocit of 0.4 cm/sec in countercurrent through the adsorber, the latter is complete freed from the remaining CH_4.

Example 4.

A further experiment is carried out with a model gas mixture, likewise not according to the invention, containing 82 % H_2, 10 % N_2 and 8 % CO. It thus does not contain any CH_4, higher hydrocarbons and CO_2. The adsorber again has an activated charcoal content of 250 ml. The model gas is introduced at 11 atmospheres. 2.67 1 of pure hydrogen flow out before the first breakthrough of N_2 appears. The pressure is then released in countercurrent and the adsorber is evacuated to 30 mm Hg. No N_2 or CO contamination in the H_2 flowing out can be detected in the following renewed adsorption stage, which has previously been subjected to a pressure equalisation with H_2 at 1

atmosphere. This is in contrast to the experiment with CH₄ in the model gas (Example 3), in which scavenging had to be carried out.

5 *Example 5.*

The experiment of Example 1 is repeated, and now the amount of H₂ recovered during the adsorption is measured. If the pressure build-up from 30 mm Hg to 1 atmosphere is carried out with part of the recovered H₂ at the end of the regeneration – as described in Example 1 – 6.58 1 of pure H₂ can be recovered during he adsorption. On subtracting the amount of hydrogen required for the pressure build-up, namely 0.62 1, this represents a yield of 5.96 1 H₂. If the pressure build-up is effected with pure hydrogen to 15 atmospheres, to the adsorption pressure, then 8.88 1 are required. Although 15.05 1 H₂ are recovered in the subsequent adsorption stage, the yield is nevertheless only 6.17 1 H₂.

Example 6.

The plant for carrying out this example consisted of a pressure adsorber containing the adsorption agent, a vacuum pump, a mass spectrometer for analysing the gases, and suitable gas inlet and outlet pipes, which were provided with automatically regulated magnetic valves. In this way it was possible to carry out cycles with alternating adsorption and desorption stages and at different cycle times over a prolonged period.

In a first series of experiments various adsorption agents were employed in this manner at an adsorption time of 3.5 minutes, a pressure release time of 3.5 minutes, and an evacuation time of 4 minutes. The adsorption pressure was 8.5 atmospheres and the end vacuum pressure was 40 mm Hg. The pressure was reinstated to 1 atmosphere with pure hydrogen before fresh coking gas was introduced. Fig. 2 shows that only the carbon molecular sieve (curve 10), which has an average micropore diameter of 0.52 nm, exhibits a sufficiently long operating life. The amount of hydrogen produced – which is the important factor – is less with a conventional activated charcoal (curve 30) than with this molecular sieve. In the case of the zeolite (curve 20) the amount of hydrogen falls markedly within a short time as the result of a catalytic effect with regard to various chemical reactions between the trace impurities in the coking gas.

Example 7.

The process described in Example 6 is repeated with the carbon molecular sieve mentioned therein, but now the cycle times are varied. For example, the adsorption times are adjusted to between 5 and 90 hours, compared with a previous time of 3.5 minutes. Figure 3 shows that the amount of hydrogen produced ovec a period of time decreases by almost half with the long cycle times (curve 50). With short cycle times (curve 40) this does not happen.

WHAT WE CLAIM IS:–

1. A process for recovering H₂ from a gas mixture which contains H₂ and CH₄, at least one of the two gases N₂ and CO and possibly one or more higher hydrocarbons, CO₂, and trace impurities by passing the gas mixture into an adsorber filled with a carbonaceous adsorption agent, in which the CH₄, and the higher hydrocarbon(s), the CO₂, and the said trace impurities, if present, are adsorbed in a first zone in the inlet region of the adsorber, and the N₂ and-or CO are adsorbed in a second zone in the outlet region of the adsorber, whereas H₂ leaves the adsorber, and in which the passage of the gas mixture to be adsorbed is interrupted at uniform time intervals for desorbing the adsorbed gases by reducing the pressure in the adsorber, the gas mixture containing not less than 5 volume % N₂ and/or CO, the change from adsorption to desorption taking place at the latest when the second zone has diminished to a length of 30 % of the overall adsorber length, but before the first breakthrough of the N₂ and/or CO, and the desorption being carried out, while the adsorber length, but before the first breakthrough of the N₂ and/or CO, and the desorption being carried out, while the adsorber outlet is closed, by evacuating the adsorber from the adsorber inlet, whereby CH₄ and the higher hydrocarbon(s) if present, the CO₂, and the said trace impurities if present, are scavenged by N₂ and/or CO desorbed in the second zone, and by unadsorbed H₂ present in the second zone.

2. A process as claimed in Claim 1, wherein the gas mixture is passed into the adsorber at elevated pressure, and desorption is carried out by pressure release followed by evacuation.

3. A process as claimed in Claim 1, or Claim 2, in which the evacuation is carried out until a pressure of 150 to 1 mm Hg is reached in the adsorber.

4. A process as claimed in Claim 3, in which the evacuation is carried out until a pressure of 50 to 10 mm Hg is reached in the adsorber.

5. A process as claimed in any of Claims 1 to 5, in which hydrogen is introduced into the adsorber after evacuation.

6. A process as claimed in any of Claims 1 to 5, in which hydrogen is introduced into the adsorber after evacuation.

7. A process as claimed in any of Claims 1 to 6, in which a carbon molecular sieve having an average micropore diameter of between 0.4 and 0.55 nm is used as the carbonaceous adsorption agent.

8. A process as claimed in Claim 7, in which the adsorption times are likewise not more than 20 minutes.

9. A process as claimed in Claim 8, in which the said times are not more than 10 minutes.

10. A process as claimed in any of Claims 7 to 9, in which a non-highly purfied coking gas (as hereinbefore defined) is used as the gas mixture.

11. A process as claimed in Claim 1, substantially as described herein with reference to Figure 1 of the accompanying drawings.

12. A process as claimed in Claim 1, substantially as described in any one of Examples 1, 2, 5, 6 or 7.

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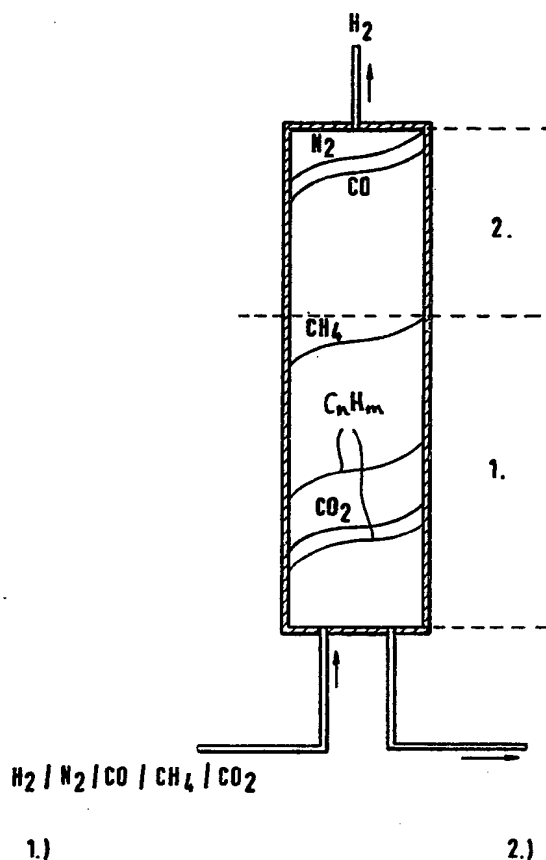57–60 Lincolns Inn Fields
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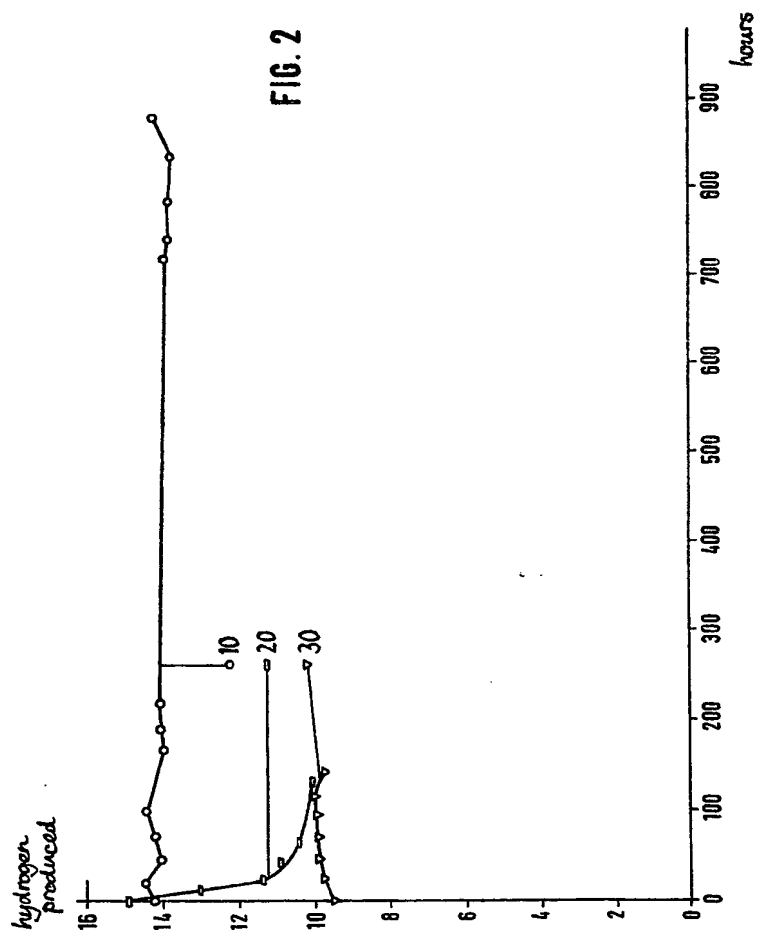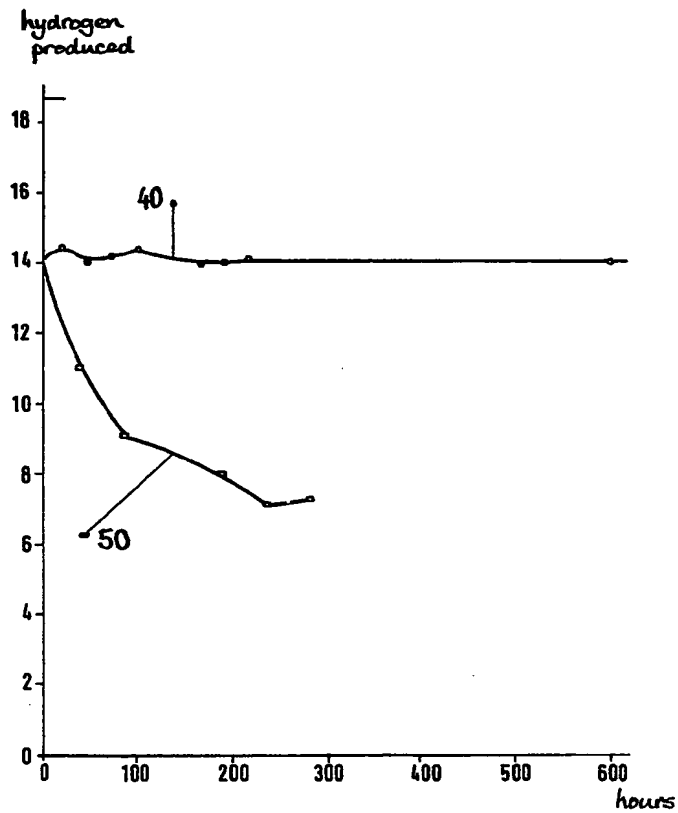*the Original on a reduced scale*
Sheet 1

FIG. 1

FIG. 2

FIG. 3

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